The Crystal Structure of Potassium Nickel(IV) Hexaoxidoiodate(VII)

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A tentative crystal structure of $KNiIO_6$ has been determined by powder diffraction methods. The elementary cell dimensions were $a = 4.969$ Å, $c = 6.000$ Å and the space group $P\,312$ (No. 149). The structure was isomorphous with that of $PbSb_2O_6$.

The hexaoxidoiodate ion and the tellurate ion can stabilize rather unusual and high oxidation states, *e.g.* Ni(IV) and Cu(III). In a study of Ni(IV) complexes, potassium nickel(IV)hexaoxidoiodate was prepared and investigated by X-ray powder diffraction methods.

EXPERIMENTAL

The compound was prepared according to a method by Ray.[1] The preparation consisted of a red, poorly crystallized powder. It was unsuited for X-ray single crystal work but gave satisfactory X-ray powder photographs even though the lines were rather broad.

The nickel content was determined gravimetrically by the dimethylglyoxime method, the iodine content by potentiometric titration with silver nitrate. (Found: Ni 18.0; I 39.4 Calc.: Ni 18.3; I 39.6).

The samples contained small amounts of water.[1] The crystal structure determination made it obvious that this water was not a part of the crystal structure but was loosely bound to the crystallite surfaces.

STRUCTURE DETERMINATION

The Guinier powder pattern could be indexed on the assumption of a hexagonal elementary cell with ·

$a = 4.969 \pm 0.005$ Å, $c = 6.000 \pm 0.005$ Å

No systematic extinctions were observed. The observed and calculated $\sin^2\theta$ values are given in Table 1. The elementary cell contained one formula unit.

Table 1. Powder diffraction data for KNiIO$_6$.

hkl	$10^4 \times \sin^2\Theta_{obs}$	$10^4 \times \sin^2\Theta_{calc}$	I_{obs}	I_{calc}
001	166	165	94	80
100	320	321	27	29
101	484	486	99	112
002	655	660	12	10
110	960	963	34	{ 31
102	976	981		{ 9
111̄) 11̄1̄)	1126	1128	24	{ 3 { 35
200	1279	1284	3	2
201	1447	1449	18	20
003	—	1486	—	1
112) 11̄2̄)	1626	1623	51	{ 37 { 22
103	1802	1807	11	13
202	1941	1944	7	6
210	2242	2246	5	3
211) 21̄1̄)	2410	2411		{ 6 { 13
			29	
113) 11̄3̄)	2448	2449		{ 10 { 3
004	2639	2642	3	4
203	2766	2770	6	9
300	2887	2888	15	13
212) 21̄2̄)	—	2907	—	{ 2 { 2
104	—	2962	—	2
301	3051	3053	6	6
302	3548	3549		{ 6
114) 11̄4̄)	3608	3609	13	{ 7 { 3
213) 21̄3̄)	3733	3732	6	{ 5 { 3
220	3853	3851	3	4

Table 2. Atomic coordinates for KNiIO$_6$. Space group P 312, No. 149.

				x	y	z
1	K	in	(*a*)	0	0	0
1	Ni	in	(*d*)	1/3	2/3	1/2
1	I	in	(*f*)	2/3	1/3	1/2
6	O	in	(*l*)	0.710	0	0.290

In order to get accurate diffraction intensities the powder pattern was recorded with a Philips X-ray diffractometer. The small elementary cell and the symmetry indicated, that this structure was built up by hexagonal closed

Table 3. Observed and calculated structure factors for KNiIO$_6$. In those cases were there is considerable overlap in the powder pattern the total intensity of a peak has been distributed according to the calculated intensities.

hkl	F_{obs}	F_{calc}	hkl	F_{obs}	F_{calc}
001	70	66	210	29	23
100	30	32	211	33	29
101	50	55	21$\bar{1}$	47	44
002	49	47	113	60	54
110	54	63	11$\bar{3}$	34	31
102	21	23	004	59	72
111	14	18	203	36	44
11$\bar{1}$	52	67	300	79	74
200	19	19	301	41	41
201	40	43	302	36	42
112	63	68	114	45	62
11$\bar{2}$	82	89	11$\bar{4}$	30	38
103	34	40	213	34	39
202	30	29	21$\bar{3}$	27	31
			220	40	48

Table 4. Bond distances in KNiIO$_6$.

K—O	2.57 Å	(6 dist.)
Ni—O	2.00 Å	(6 dist.)
I—O	2.00 Å	(6 dist.)

packed layers of oxygen atoms while the iodide, nickel and potassium ions occupied the octahedral holes between the layers.

For a preliminary discussion it is useful to assume that the potassium nickel(IV) hexaoxidoiodate(VII) is built up by O^{2-}, K^+, Ni^{4+}, and I^{7+} ions. If, then, the three positive ions are equivalent from the geometrical point of view, this structure can be isomorphous with the cadmium iodide structure. Although there is a clear resemblance between the intensities of cadmium hydroxide, for instance, and those of the present structure, it is more probable that the structure is isomorphous with the niobite ($FeNb_2O_6$), the "threerutile" ($ZnSb_2O_6$), or the lead metantimonate ($PbSb_2O_6$) structure.[3] The first two can immediately be ruled out since they do not contain the same symmetry elements as the investigated structure. The lead metantimonate structure, on the other hand, fulfills the symmetry conditions and, moreover, in this structure type the three positive ions may occupy crystallographically different positions.

In a first attempt the potassium ions replaced the lead ion, while the nickel and iodine atoms replaced the antimony atoms in the metantimonate structure. The arrangement of oxygen atoms was assumed to be the same in the two structures. A comparison between observed and calculated structure factors showed satisfactory agreement. The atomic parameters can be found in Table 2,
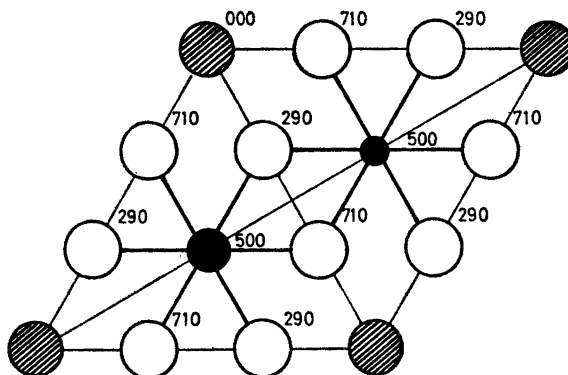
Fig. 1. Projection of the crystal structure of KNiIO$_6$ on (001).

comparison between F_o and F_c in Table 3. The R-factor $(||F_o| - |F_c||/|F_o|)$ was found equal to 0.13.

It is rather meaningless to refine this structure by least squares methods, since it is impossible to distinguish between the intensities due to the *hkl* and the *khl* planes. This means that it is impossible to distinguish between the nickel atom position 1/3 2/3 1/2 and the iodine atom position 2/3 1/3 1/2. However, the distances Ni(IV)—O and I(VIII)—O are certainly about equal, so that the limitation mentioned has no serious influence on the general structure determination.

DESCRIPTION OF THE TENTATIVE STRUCTURE

The structure of KNiIO$_6$ can be described in the following way. The oxygen atoms form a hexagonal close packed structure. Of the layers of octahedral holes (between successive oxygen layers), every second one is occupied by nickel and iodine atoms, leaving one third of the holes in this layer empty. The empty holes are regularly distributed and next to each empty hole, the remaining potassium ions are situated in the next layer above or below, see Fig. 1.

REFERENCES

1. Ray, P. In Moeller, T. *Inorg. Syn.* 5 (1957) 202.
2. Magnéli, A. *Arkiv Kemi, Mineral. Geol.* 15 (1942) No. 3.
3. Wells, A. F. *Structural Inorganic Chemistry*, 3rd Ed., Oxford 1962, pp. 679—680.